Energy and Structure of Dithiophosphinate Complexes with Trivalent Actinides and Lanthanides: Computational and Experimental Studies

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Separation of trivalent actinides from lanthanides has been a challenging subject of study in recent years due to the demand in the treatment of nuclear wastes. Bis(2,4,4-trimethylpentyl)dithiophosphinic acid, a commercially available dithiophosphinic acid (DTP), has been shown to be highly selective in the solvent extraction of An(III) over Ln(III). Various attempts have been made to reveal the fundamental chemical principles underlying the selectivity. In this study, Density Functional Theory (DFT) calculations were performed on the complexation of a smaller DTP, $(CH_3)_2P(S)SH$, with Am(III) and lighter Ln(III) (La^{3+}, Nd^{3+} and Eu^{3+}), using Stuggart small core relativistic effective core potentials and including the spin-orbit effects. The energy and structure of the hydrated and unhydrated complexes were calculated and compared. For the trivalent lanthanides, the energy of monohydrated DTP complexes, $Ln(DTP)_4 \cdot H_2O$, is lower than that of unhydrated complexes, $Ln(DTP)_4$. However, for americium(III), the unhydrated complex, $Am(DTP)_4$, has lower energy than the hydrated one. The computational results are consistent with experimental observations by spectroscopic techniques including FT-IR, TRLFS and ES/MS, suggesting that the difference in the degree of hydration between the Ln(III) and An(III) complexes contributes to the selectivity of DTP for An(III) over Ln(III) in solvent extraction.

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